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EP-A- 0 238 241
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CHEMICAL ABSTRACTS, vol. 107, no. 18, November 1987 Columbus, Ohio, USA J.IMANARI et al.: "Dielectric ceramic composition" page 868; left-hand column; ref. no. 16105C & JP-A-6237804

CHEMICAL ABSTRACTS, vol. 108, no. 6, February 1988 Columbus, Ohio, USA H.TAMURA: "Dielectric ceramic composition for high-frequency use" page 671; right-hand column; ref. no. 47724C & JP-A-A62115817

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Description

This invention relates to a dielectric ceramic composition for a multi-layer capacitor comprising internal electrodes mainly containing Cu or Cu alloys and dielectric layers mainly containing Pb based perovskite ceramics; it paticularly relates to a composition having a small temparature coefficient of capacitance which is in the range of the Y-class B-characteristics of the JIS (Japanese Industrial Standard) and which has a temperature change ratio variation from -25°C to 85°C within ±10% based on a value of 20°C.

Recently, multi-layer capacitors have been mainly used in the electric circuits of various electric products to meet the need for small-sized and large-capacitance capacitors. Such multi-layer capacitors are usually made by co-sintering internal electrodes and a dielectric ceramic body. Conventionally, a ceramic composition comprising a barium titanate system is widely used as a dielectric material for a ceramic capacitor having a high dielectric constant. However, since such barium titanate ceramics are sintered at a temparature as high as about 1300°C, it is required to use metals such as Pd, Pt and the like which have a high cost and a high electric resistance, for internal electrodes of multi-layer capacitors. Further, owing to the inferiority in DC bias and signal voltage characteristics, dielectric layers of barium titanate ceramics can not get thinner in order to make a capacitor small-sized and having a large capacitance.

Therefore, there is now strongly requested a multi-layer capacitor comprising internal electrodes made of Cu being of low costs and having a low electric resistance and of dielectric layers made of Pb based perovskite ceramics having a good voltage characteristic and a low sintering temparature. We have also proposed a dielectric ceramic composition which has practical electric characteristics and is able to be sintered together with Cu, that is, sintered at a condition in which Cu can not be melted and not be oxydized. Furthermore, we have proposed a method by which the above multi-layer capacitor can be mass-produced. Therefore, the multi-layer capacitor comes to be of good commercial costs and to have larger capacitance although it is small-sized, so that electrolytic capacitors can be replaced by the multi-layer capacitors.

However, the multi-layer capacitor proposed up to the present time has poorer characteristics referring to the temparature coefficient of capacitance (corresponding to JIS Y E characteristics), so that the thus produced capacitor can be used only to a limited extent. Therefore, it is desired to develop a superior capacitor that has a large capacitance which meets the above Y B-characteristics, i.e. has a temparature change ratio from -25°C to 85°C within ±10% based on a value of 20°C. However, there has not yet been devoloped a capacitor having a practical level in CR product, voltage characteristic and the like.

Therefore, the first object of the present invention is to provide a dielectric ceramic composition for multi-layer capacitors which meet the above requirements.

Further, the second object of the present invention is to provide a multi-layer capacitor which meet the above requirements.

These objects are attained by a dielectric ceramic composition as defined in claim 1 and a multi layer ceramic capacitor as defined in claim 3.

In accordance with this invention, there is provided a dielectric ceramic composition essentially consisting of one or more substances selected from those represented by the following formulas:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are in the scope enclosed by 5 points A(x=0.07, y=0.15), B(x=0.07, y=0.07), C(x=0.16, y=0.07), D(x=0.24, y=0.22) and E(x=0.16, y=0.22); and $0 \leqq a \leqq 0.1$, $0.02 \leqq b \leqq 1.0$, $0.002 \leqq bz \leqq 0.04$ as shown in Fig.1;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y is in the scope enclosed by 5 points A(x=0.07, y=0.14), B(x=0.07, y=0.08), C(x=0.18, y=0.08), D(x=0.24, y=0.22) and E(x=0.16, y=0.22); and $0 \leqq a \leqq 0.1$, $0.02 \leqq b \leqq 1.0$, $0.002 \leqq bz \leqq 0.04$ as shown in Fig.2;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are in the scope enclosed by 5 points A(x=0.07, y=0.16), B(x=0.07, y=0.09), C(x=0.19, y=0.09), D(x=0.24, y=0.22) and E(x=0.16, y=0.22); and $0 \leqq a \leqq 0.1$, $0.02 \leqq b \leqq 1.0$, $0.002 \leqq bz \leqq 0.04$ as shown in Fig.3;

In the dielectric ceramic composition according to the invention, it is preferred that at most 85% of the Cu atoms included therein are substituted by Mn atoms, since the absolute insulation resistivity is increased.

According to the above inventive dielectric ceramic composition, the amount of A site in the perovskite phase represented by the formula ABO_3 is over the stoichiometric amount, so that the insulation resistivity is not lowered even if the composition has been sintered under a low oxygen partial pressure. Futhermore, the B site of the perovskite phase contains Cu, so that the composition can be sintered at a lower temparature and becomes to have a small temparature coefficient of dielectric constant.

In accordance with this invention, therefore, there is also provided a multi-layer capacitor comprising dielectric ceramic layers essentially consisting of one or more substances selected from those represented by the above formulas (1), (2) and (3).

Fig.1 is a composition diagram of

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

in accordance with the present invention.

Fig.2 is a composition diagram of

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

in accordance with the present invention.

Fig.3 is a composition diagram of

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

in accordance with the present invention.

The composition herein may be prepared in accordance with various well-known ceramic procedures.

EXAMPLE 1

A multi-layer ceramic capacitor which meets the JIS Y-class B-characteristics with respect to the capacitance variation depending on temparature changes (a temparature coeffieient of capacitance) was prepared according to the following method.

The starting materials, viz. lead oxide (PbO), strontium carbonate ($SrCO_3$), barium carbonate ($BaCO_3$), zinc oxide (ZnO), niobium oxide (Nb_2O_5), titanium oxide (TiO_2) and copper oxide (CuO), all chemically pure grade, were used. After compensated as to pure contents, they were weighted out to compose a substance represented by the following formula:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x, y, z, a and b may be optional values.

They were mixed in a ball mill with zirconia 4mmØ balls and with distilled water for 17 hours. Thereafter, the mixture was dried and charged into a crucible made of alumina which is closed by an alumina lid and then calcined at 750~900 °C. The calcined mixture was crushed and ground in a ball mill for 17 hours by using the same solvent and balls as the above.

To the sufficiently dried dielectric powder, 5 wt% of polyvinyl butylal resin with 70 wt% of a solvent based on the dielectric powder weight was added and mixed in a ball mill. The resulting mixture was brought into a sheet form by a docter- blade method.

Cu_2O powder having an average particle size of 0.8μm was mixed with 0.5 wt% of ethylcellose and 25 wt% of a solvent based on the Cu_2O weight to obtain an electrode paste. The paste was printed on the dielectric sheet by means of screen printing. The printed sheet was laminated and then was cut into a predetermined size. The number of dielectric layers was set to 20.

The laminated body thus obtained was heated for 6 hours at 500 °C, and organic components were burned out. Thereafter, the laminated body was heated in a N_2 gas flow containing 1% of H_2 for 8 hours at 450 °C and the internal electrode thereof was reduced.

Sintering was carried out by charging the laminated body into a magnesia vessel together with a large volume of the calcinated dielectric powder and also controlling the oxygen partial pressure in a atmosphere so that the internal electrode could not be oxydized absolutely by gas supply of CO_2, CO, H_2, O_2, N_2 and

the like and then maintaining a predetermined temparature for 2 hours. As the sintering temparature is varied depending on the composition of a calcinated dielectric powder, it is prefered to choose a temparature in which the largest density can be obtained when the pressed body is fired at various temperature.

500 pieces of ceramic body were produced in one sintering process. On the ends of the resulting ceramic bodies, Cu paste was baked to form an external electrode to form a multi-layer capacitor.

The size of the multi-layers capacitor is 3.2 × 1.6 × 0.9mm, the thickness of the electrode layers is about 2μm and each thickness of the dielectric layers is about 20μm.

The capacitance and tanδ (the dielectric loss) of the multi-layer capacitor were measured under the conditions of 1V and 1kHz. The insulated resistivity was measured after one minute with 20V being applied. The effective area of the electrode and the thickness of the dielectric layer were measured after polishing the capacitor and then the dielectric constant and the insulation resistivity of the dielectric layer were calculated. Each of the properties was recorded as an average value of good samples.

In the Table 1 below, there are shown: x, y, z, a and b values of the dielectric composition; optimum sintering temparature; dielectric constant of the dielectric layer at 20 °C; tanδ ; resistivity; and temparature change ratio of the dielectric constant.

As shown in the Table 1, the compositions outside the polygon A,B,C,D,E scope shown in Fig.1 were not suitable for ceramic capacitor materials since they lack at least one property of (1) a sintering temparature of below 1000 °C, (2) a dielectric constant of above 2000, (3) a resistivity of above $10^{+12}\Omega$ cm and (4) a temparature change ratio of capacitance meeting the YB characteristics of the JIS. Thus, the comparative compositions are excluded from the scope of the present invention.

It is also taught by the data in the Table 1 that the sintering temparature can be lowered and the insulation resistivity can be increased by providing an excess content (a) of the A site of more than zero in the perovskite phase represented by the formula $A_{1+a}BO_3$ of the dielectric layer.

Table 1

No.	Composition					
	Me	x	y	z	a	b
1 #	Sr	0.06	0.15	0.02	0.02	0.333
2	Sr	0.07	0.15	0.02	0.02	0.333
3	Sr	0.07	0.07	0.02	0.02	0.333
4 #	Sr	0.1	0.18	0.02	0.02	0.333
5 #	Sr	0.1	0.12	0.003	0.02	0.333
6	Sr	0.1	0.12	0.006	0.02	0.333
7	Sr	0.1	0.12	0.02	0.02	0.333
8	Ba	0.1	0.12	0.02	0.02	0.333
9	Sr	0.1	0.12	0.12	0.02	0.333
10 #	Sr	0.1	0.12	0.14	0.02	0.333
11 #	Sr	0.1	0.06	0.02	0.02	0.333
12	Sr	0.16	0.22	0.02	0.02	0.333
13 #	Sr	0.16	0.15	0.02	-0.01	0.333
14	Sr	0.16	0.15	0.02	0	0.333
15	Sr	0.16	0.15	0.02	0.02	0.333
16	Ba	0.16	0.15	0.02	0.02	0.333
17	Sr	0.16	0.15	0.02	0.1	0.333
18 #	Sr	0.16	0.15	0.02	0.12	0.333
19	Sr	0.16	0.07	0.02	0.02	0.333
20 #	Sr	0.2	0.24	0.02	0.02	0.333
21 #	Sr	0.2	0.18	0.444	0.02	0.015
22	Sr	0.2	0.18	0.333	0.02	0.02
23	Sr	0.2	0.18	0.02	0.02	0.333
24	Ba	0.2	0.18	0.02	0.02	0.333
25	Sr	0.2	0.18	0.007	0.02	0.95
26 #	Sr	0.2	0.12	0.02	0.02	0.333
27	Sr	0.24	0.24	0.02	0.02	0.333

: comparative sample

Table 1 (continued)

No.	Optimum Sintering Temperature (℃)	Dielectric Properties ε	tanδ %	Insulation Resistivity $10^{12}\Omega$ cm	$\Delta\varepsilon/\varepsilon$ (20℃) -25℃ %	+85℃ %
1 #	860	2100	0.70	1.0	-12	-11
2	860	2000	0.70	1.5	-9	-9
3	920	2050	0.80	1.2	-9	-8
4 #	880	4300	0.35	3.0	-7	-11
5 #	960	4000	0.25	7.5	-12	-13
6	960	3750	0.30	5.5	-8	-9
7	900	3550	0.50	2.0	-7	-7
8	920	3900	0.65	2.0	-8	-8
9	840	3400	0.70	1.0	-6	-6
10 #	840	3150	0.90	0.2	-5	-6
11 #	920	1950	0.60	1.5	-7	-8
12	900	4050	0.20	15	-5	-6
13 #	1020	4850	0.60	6.0	-12	-13
14	980	4150	0.55	4.5	-10	-9
15	940	3650	0.30	12	-4	-5
16	960	4050	0.45	13	-7	-7
17	920	3200	0.15	1.0	-4	-4
18 #	920	3050	0.15	0.3	-3	-4
19	980	2150	0.35	10	-4	-5
20 #	940	3800	0.10	30	-3	-12
21 #	1020	3650	0.05	40	-8	-11
22	1000	3600	0.10	35	-8	-9
23	960	2600	0.20	25	-3	-8
24	960	3050	0.30	20	-5	-9
25	940	2400	0.35	11	-3	-7
26 #	1020	1800	0.30	20	-3	-7
27	980	2100	0.05	35	-1	-10

: comparative example

EXAMPLE 2

The composition herein is characterized in that part of the Cu component in the perovskite of the dielectric layer was substituted by Mn.

A dielectric powder was prepared to have a composition represented by the following formula:

(1)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15} \cdot ((Cu_{1-c}Mn_c)_{1/3}Nb_{2/3})_{0.02}\}O_{3.02}$

wherein c is optional and therefrom a multi-layer capacitor was made by the same method as Example 1. Evaluation tests on various properties of the resultant capacitor were carried out by the same method as Example 1.

In the Table 2 below, there are shown a substituted amount (c) of Mn and each value of various properties.

As shown in the Table 2, the insulation resistivity can be increased by subsutituting part of the Cu component in the perovskite of the dielectric layer by Mn. However, as the content of Mn becomes over 85%, the temparature change ratio of capacitance becomes too large to meet the YB characteristics of the JIS. Therefore, such compositions are excluded from the present invention.

Table 2

No.	Composition (°C)	Optimum Sintering Temperature (°C)	dielectric properties $\Delta\epsilon/\epsilon$ (20°C)				
			ϵ	tanδ %	insulation resistivity $10^{12}\Omega$ cm	-25°C %	+85°C %
1	0.0	940	3650	0.30	12	-4	-5
2	0.1	940	3850	0.25	20	-5	-7
3	0.3	940	4050	0.25	25	-6	-8
4	0.85	960	4150	0.20	30	-8	-9
5 #	0.90	960	4300	0.20	35	-11	-14

: comparative example

EXAMPLE 3

According to the same procedure as Example 1, a multi-layer capacitor was prepared.

The starting materials, viz. lead oxide(PbO), strontium carbonate($SrCO_3$), barium carbonate($BaCO_3$), zinc oxide(ZnO), niobium oxide(Nb_2O_5), titanium oxide(TiO_2), tantalum oxide(Ta_2O_3) and copper oxide-(CuO), all chemically pure grade, were used. After compensated as to pure contents, they were measured in a amount to compose a substance represented by the following formula:

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x, y, z, a and b may be optional values.

Various properties of the resultant capacitor were measured according to the same method and conditions, and each typical data thereof was recorded as an average value of good samples.

In the Table 3 below, there are shown: x, y, z, a and b values of the dielectric composition; optimum sintering temparature; dielectric constant of the dielectric layer at 20°C ; tanδ ; resistivity; and temparature change ratio of the dielectric constant.

As shown in the Table 3, the compositions outside the polygon A,B,C,D,E scope shown in Fig.2 were not suitable for ceramic capacitor materials since they lack at least one property of (1) a sintering temparature of below 1000°C, (2) a dielectric constant of above 2000, (3) a resistivity of above $10^{+12}\Omega$ cm and (4) a temparature coefficient of capacitance meeting the YB characteristics of the JIS. Then, the compositions are excluded from the scope of the present invention.

It is also taught by the data in the Table 3 that the sintering temparature can be lowered and the insulation resistivity can be increased by providing an excess content (a) of the A site of more than zero in the perovskite phase represented by the formula $A_{1+a}BO_3$ of the dielectric layer.

Table 3

No.	Composition					
	Me	x	y	z	a	b
1 #	Sr	0.06	0.14	0.02	0.02	0.333
2	Sr	0.07	0.14	0.02	0.02	0.333
3	Sr	0.07	0.08	0.02	0.02	0.333
4 #	Sr	0.1	0.18	0.02	0.02	0.333
5 #	Sr	0.1	0.12	0.003	0.02	0.333
6	Sr	0.1	0.12	0.006	0.02	0.333
7	Sr	0.1	0.12	0.02	0.02	0.333
8	Ba	0.1	0.12	0.02	0.02	0.333
9	Sr	0.1	0.12	0.12	0.02	0.333
10 #	Sr	0.1	0.12	0.14	0.02	0.333
11 #	Sr	0.1	0.07	0.02	0.02	0.333
12	Sr	0.16	0.22	0.02	0.02	0.333
13 #	Sr	0.16	0.14	0.02	-0.01	0.333
14	Sr	0.16	0.14	0.02	0	0.333
15	Sr	0.16	0.14	0.02	0.02	0.333
16	Ba	0.16	0.14	0.02	0.02	0.333
17	Sr	0.16	0.14	0.02	0.1	0.333
18 #	Sr	0.16	0.14	0.02	0.12	0.333
19	Sr	0.18	0.08	0.02	0.02	0.333
20 #	Sr	0.21	0.23	0.02	0.02	0.333
21 #	Sr	0.21	0.18	0.444	0.02	0.015
22	Sr	0.21	0.18	0.333	0.02	0.02
23	Sr	0.21	0.18	0.02	0.02	0.333
24	Ba	0.21	0.18	0.02	0.02	0.333
25	Sr	0.21	0.18	0.007	0.02	0.95
26 #	Sr	0.21	0.12	0.02	0.02	0.333
27	Sr	0.24	0.22	0.02	0.02	0.333

: comparative sample

Table 3 (continued)

No.	Optimum Sintering Temperature (℃)	Dielectric Properties ε	tanδ %	Insulation Resistivity $10^{12}\Omega$ cm	Δε/ε (20℃) -25℃ %	+85℃ %
1 #	880	2300	0.85	0.6	-14	-12
2	880	2200	0.80	1.2	-10	-9
3	940	2150	0.85	1.2	-9	-9
4 #	900	4650	0.50	2.5	-9	-13
5 #	1000	4400	0.30	6.5	-16	-13
6	980	3850	0.40	5.0	-9	-10
7	920	3650	0.50	1.5	-8	-8
8	940	4050	0.80	1.8	-9	-8
9	880	3550	0.75	1.0	-7	-6
10 #	860	3200	1.20	0.15	-6	-7
11 #	960	2100	0.85	1.0	-9	-10
12	900	4050	0.25	12	-6	-6
13 #	1040	5000	0.70	0.6	-14	-15
14	980	4200	0.60	4.0	-10	-10
15	960	3750	0.40	10	-4	-4
16	980	4100	0.45	10	-7	-8
17	940	3300	0.25	1.0	-5	-6
18 #	960	3250	0.15	0.2	-4	-4
19	980	2250	0.45	8	-4	-6
20 #	980	4050	0.25	22	-2	-19
21 #	1040	3800	0.15	33	-10	-13
22	1000	3750	0.20	30	-9	-9
23	980	2700	0.30	20	-4	-8
24	980	3150	0.45	13	-7	-9
25	960	2550	0.40	7	-4	-9
26 #	1040	2000	0.35	15	-6	-8
27	1000	2250	0.10	25	-2	-10

: comparative example

EXAMPLE 4

The composition herein is characterized in that a part of the Cu component in the perovskite of the dielectric layer was substituted by Mn.

A dielectric powder was prepared to have a composition represented by the following formula:

(2)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15} \cdot ((Cu_{1-c}Mn_{c})_{1/3}Ta_{2/3})_{0.02}\}O_{3.02}$

wherein c is optional and therefrom a multi-layer capacitor was made by the same method as Example 3. Evaluation tests on various properties of the resultant capacitor were carried out by the same method as Example 1.

In the below Table 4, there are shown a substituted amount (c) of Mn and each value of various properties.

As shown in the Table 4, the insulation resistivity can be increased by subsututiting part of the Cu component in the perovskite of the dielectric layer by Mn. However, as the content of Mn becomes over 85%, the temparature change ratio of capacitance becomes too large to meet the YB characteristics of the JIS. Therefore, such compositions are excluded from the present invention.

Table 4

No.	Composition (°C)	Optimum Sintering Temperature (°C)	Dielectric Properties $\Delta\epsilon/\epsilon$ (20°C)				
			ϵ	tanδ %	Insulation Resistivity $10^{12}\Omega$ cm	-25°C %	+85°C %
1	0.0	960	3750	0.40	10	-4	-4
2	0.1	960	3900	0.35	15	-5	-6
3	0.3	960	4150	0.30	18	-7	-8
4	0.85	980	4200	0.30	27	-9	-9
5 #	0.90	1000	4400	0.25	30	-12	-15

: comparative example

EXAMPLE 5

According to the same procedure as Example 1, a multi-layer capacitor was prepared.

The starting materials, viz. lead oxide(PbO), strontium carbonate($SrCO_3$), barium carbonate($BaCO_3$), zinc oxide(ZnO), niobium oxide(Nb_2O_5), titanium oxide(TiO_2), tungsten oxide(W_2O_3) and copper oxide-(CuO), all chemically pure grade, were used. After compensated as to pure contents, they were measured in a amount to compose a substance represented by the following formula:

(3) $Pb_{1-x+a}Me_{x}\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_{y}(Cu_{b}W_{1-b})_{z}\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x, y, z, a and b may be optional values.

Various properties of the resultant capacitor were measured according to the same method and conditions, and each typical data thereof was recorded as an average value of good samples.

In the below Table 5, there are shown: x, y, z, a and b values of the dielectric composition; optimum sintering temparature; dielectric constant of the dielectric layer at 20°C; tanδ; resistivity; and temparature change ratio of the dielectric constant.

As shown in the Table 5, the compositions outside the polygon A,B,C,D,E scope shown in Fig.3 were not suitable for ceramic capacitor materials since they lack at least one property of (1) a sintering temparature of below 1000°C, (2) a dielectric constant of above 2000, (3) a resistivity of above $10^{+12}\Omega$ cm and (4) a temparature coefficient of capacitance meeting the YB characteristics of the JIS. Then the compositions are exclused from the scope of the present invention.

It is also taught by the data in the Table 5 that the sintering temparature can be lowered and the insulation resistivity can be increased by providing an excess content (a) of the A site of more than zero in the perovskite phase represented by the formula $A_{1+a}BO_3$ of the dielectric layer.

Table 5

No.	Composition					
	Me	x	y	z	a	b
1 #	Sr	0.06	0.16	0.02	0.02	0.5
2	Sr	0.07	0.16	0.02	0.02	0.5
3	Sr	0.07	0.09	0.02	0.02	0.5
4 #	Sr	0.1	0.19	0.02	0.02	0.5
5 #	Sr	0.1	0.14	0.002	0.02	0.5
6	Sr	0.1	0.14	0.004	0.02	0.5
7	Sr	0.1	0.14	0.02	0.02	0.5
8	Ba	0.1	0.14	0.02	0.02	0.5
9	Sr	0.1	0.14	0.08	0.02	0.5
10 #	Sr	0.1	0.14	0.10	0.02	0.5
11 #	Sr	0.1	0.08	0.02	0.02	0.5
12	Sr	0.16	0.22	0.02	0.02	0.5
13 #	Sr	0.16	0.16	0.02	-0.01	0.5
14	Sr	0.16	0.16	0.02	0	0.5
15	Sr	0.16	0.16	0.02	0.02	0.5
16	Ba	0.16	0.16	0.02	0.02	0.5
17	Sr	0.16	0.16	0.02	0.1	0.5
18 #	Sr	0.16	0.16	0.02	0.12	0.5
19	Sr	0.19	0.09	0.02	0.02	0.5
20 #	Sr	0.22	0.23	0.02	0.02	0.5
21 #	Sr	0.22	0.2	0.667	0.02	0.015
22	Sr	0.22	0.2	0.5	0.02	0.02
23	Sr	0.22	0.2	0.02	0.02	0.5
24	Ba	0.22	0.2	0.02	0.02	0.5
25	Sr	0.22	0.2	0.011	0.02	0.95
26 #	Sr	0.22	0.14	0.02	0.02	0.5
27	Sr	0.24	0.22	0.02	0.02	0.5

: comparative sample

Table 5 (continued)

No.	Dielectric Properties				Δε/ε (20℃)	
	Optimum Sintering Temperature (℃)	ε	tanδ %	Insulation Resistivity 10^{12}Ω cm	-25℃ %	+85℃ %
1 #	840	2200	0.60	0.8	-12	-10
2	840	2100	0.60	1.2	-9	-8
3	880	2050	0.80	1.0	-8	-7
4 #	860	4000	0.30	2.0	-8	-12
5 #	940	3950	0.35	7.0	-11	-13
6	920	3650	0.35	4.5	-7	-8
7	860	3500	0.40	1.8	-7	-6
8	860	3750	0.60	2.0	-8	-7
9	820	3250	0.75	1.2	-5	-4
10 #	820	3000	1.02	0.2	-4	-5
11 #	880	1900	0.50	1.0	-8	-7
12	880	3900	0.20	12	-6	-6
13 #	1020	4650	0.75	0.8	-11	-13
14	960	4050	0.55	4.0	-9	-9
15	900	3400	0.30	8	-4	-5
16	920	3950	0.45	11	-8	-7
17	880	3050	0.20	1.2	-3	-4
18 #	880	2800	0.20	0.2	-3	-3
19	940	2100	0.30	7	-5	-6
20 #	900	3550	0.10	25	-2	-14
21 #	1020	3450	0.05	30	-7	-13
22	980	3500	0.10	25	-7	-10
23	940	2400	0.30	19	-3	-7
24	960	2850	0.20	15	-6	-8
25	900	2250	0.25	9	-3	-7
26 #	1020	1600	0.35	17	-3	-8
27	940	2050	0.10	30	0	-9

: comparative example

EXAMPLE 6

The composition herein is characterized in that part of the Cu component in the perovskite of the dielectric layer was substituted by Mn.

A dielectric powder was prepared to have a composition represented by the following formula:

(3)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15} \bullet ((Cu_{1-c}Mn_c)_{1/2}W_{1/2})_{0.02}\}O_{3.02}$

wherein c is optional and therefrom a multi-layer capacitor was made by the same method as Example 5. Evaluation tests on various properties of the resultant capacitor were carried out by the same method as Example 1.

In the below Table 6, there are shown a substituted amount (c) of Mn and each value of various properties.

As shown in the Table 6, the insulation resistivity can be increased by subsutituting part of the Cu component in the perovskite of the dielectric layer by Mn. However, as the content of Mn becomes over 85%, the temparature change ratio of capacitance becomes too large to meet the YB characteristics of the JIS. Therefore, such compositions are excluded from the present invention.

As apparent from the above description, by use of the multi-layer capacitor in accordance with the present invention the material costs for the electrodes are remarkably lowered, and superior properties can be obtained especially in a high frequency circuit. Further, the use of Pb based dielectric materials makes it possible to render dielectric layers thinner for multi-layer capacitors, so that there can be provided a small sized capacitor having a larger capacitance for replacement of conventional electrolytic capacitor. Furthermore, the temparature coefficient of capacitance sufficiently meets the YB characteristics of the JIS, so that its utilized circuit field can be expanded further.

Table 6

No.	Composition (°C)	Optimum Sintering Temperature (°C)	Dielectric Properties $\Delta\epsilon/\epsilon$ (20°C)				
			ϵ	tanδ %	Insulation Resistivity $10^{12}\Omega$ cm	-25°C %	+85°C %
1	0.0	900	3400	0.30	8	-4	-5
2	0.1	900	3650	0.25	15	-4	-6
3	0.3	900	3800	0.25	20	-5	-8
4	0.85	920	3900	0.15	25	-7	-9
5 #	0.90	920	4150	0.15	30	-10	-14

: comparative example

Claims

1. Dielectric ceramic composition consisting essentially of one or more substances selected from substances represented by the following formulas:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are within the polygon scope enclosed by 5 points A(x = 0.07, y = 0.15), B(x = 0.07, y = 0.07), C(x = 0.16, y = 0.07), D(x = 0.24, y = 0.22) and E(x = 0.16, y = 0.22); and $0 \leq a \leq 0.1$, $0.02 \leq b \leq 1.0$, $0.002 \leq bz \leq 0.04$;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are with in the polygon scope enclosed by 5 points A(x = 0.07, y = 0.14), B(x = 0.07, y = 0.08), C(x = 0.18, y = 0.08), D(x = 0.24, y = 0.22) and E(x = 0.16, y = 0.22); and $0 \leq a \leq 0.1$, $0.02 \leq b \leq 1.0$, $0.002 \leq bz \leq 0.04$;

(3) $Pb_{1-x-a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are with in the polygon scope enclosed by 5 points A(x = 0.07, y = 0.16), B(x = 0.07, y = 0.09), C(x = 0.19, y = 0.09), D(x = 0.24, y = 0.22)

and E(x = 0.16, y = 0.22); and O≦a≦0.1, 0.02≦b≦1.0, 0.002≦bz≦0.04.

2. Dielectric ceramic composition according to claim 1, wherein at most 85% of Cu atoms included therein are substituted by Mn atoms.

3. A multi layer ceramic capacitor principally made up of (a) internal electrode layers mainly containing Cu or Cu alloys and (b) dielectric layers mainly containing at least one ceramic substance selected from substances represented by the following formulas:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y is in the scope enclosed by 5 points A(x = 0.07, y = 0.15), B(x = 0.07, y = 0.07), C(x = 0.16, y = 0.07), D(x = 0.24, y = 0.22) and E(x = 0.16, y = 0.22); and O≦a≦0.1, 0.02≦b≦1.0, 0.002≦bz≦0.04;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y are with in the polygon scope enclosed by 5 points A(x = 0.07, y = 0.14), B(x = 0.07, y = 0.08), C(x = 0.18, y = 0.08), D(x = 0.24, y = 0.22) and E(x = 0.16, y = 0.22); and O≦a≦0.1, 0.02≦b≦1.0, 0.002≦bz≦0.04;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

wherein Me is at least one element selected from Sr and Ba; x and y is in the scope enclosed by 5 points A(x = 0.07, y = 0.16), B(x = 0.07, y = 0.09), C(x = 0.19, y = 0.09), D(x = 0.24, y = 0.22) and E(x = 0.16, y = 0.22); and O≦a≦0.1, 0.02≦b≦1.0, 0.002≦bz≦0.04.

4. A multi layer ceramic capacitor according to claim 3, wherein at most 85% of Cu atoms included in the dielectric layers are substituted by Mn atoms.

Patentansprüche

1. Dielektrische Keramikzusammensetzung, bestehend im wesentlichen aus einer oder mehreren Substanzen, ausgewählt aus Substanzen, die durch die folgenden Formeln wiedergegeben werden:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,15), B (x = 0,07, y = 0,07), C (x = 0,16, y = 0,07), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,14), B (x = 0,07, y = 0,08), C (x = 0,18, y = 0,08), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,16), B (x = 0,07, y = 0,09), C (x = 0,19, y = 0,09), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04.

2. Dielektrische Keramikzusammensetzung nach Anspruch 1, wobei höchstens 85 % der enthaltenen Cu-Atome durch Mn-Atome substituiert sind.

3. Vielschicht-Keramikkondensator, im wesentlichen aufgebaut aus (a) inneren Elektrodenschichten, die hauptsächlich Cu oder Cu-Legierungen enthalten und (b) dielektrischen Schichten, die hauptsächlich mindestens eine Keramikverbindung enthalten, ausgewählt aus Substanzen, die durch die folgenden Formeln wiedergegeben werden:

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,15), B (x = 0,07, y = 0,07), C (x = 0,16, y = 0,07), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,14), B (x = 0,07, y = 0,08), C (x = 0,18, y = 0,08), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$,

wobei Me mindestens ein Element darstellt, ausgewählt aus Sr und Ba; und x und y innerhalb der Polygonfläche liegen, die eingeschlossen wird von den 5 Punkten A (x = 0,07, y = 0,16), B (x = 0,07, y = 0,09), C (x = 0,19, y = 0,09), D (x = 0,24, y = 0,22) und E (x = 0,16, y = 0,22); und wobei O ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04.

4. Vielschicht-Keramikkondensator nach Anspruch 3, wobei höchstens 85 % der enthaltenen Cu-Atome durch Mn-Atome substituiert sind.

Revendications

1. Composition céramique diélectrique consistant essentiellement en une ou plusieurs substances sélectionnées parmi celles représentées par les formules suivantes :

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba ; x et y sont dans le domaine polygonal délimité par 5 points A (x = 0,07, y = 0,15), B (x = 0,07, y = 0,07), C (x = 0,16, y = 0,07), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04 ;

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba ; x et y sont dans le domaine polygonal délimité par 5 points A (x = 0,07, y = 0,14), B (x = 0,07, y = 0,08), C (x = 0,18, y = 0,08), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04 ;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba ; x et y sont dans le domaine polygonal délimité par 5 points A (x = 0,07, y = 0,16), B (x = 0,07, y = 0,09), C (x = 0,19, y = 0,09), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04.

2. Composition de céramique diélectrique selon la revendication 1, dans le contenu de laquelle au plus 85 % des atomes de Cu sont remplacés par des atomes de Mn.

3. Condensateur en céramique à plusieurs couches constitué principalement par (a) des couches internes d'électrodes contenant surtout du cuivre ou des alliages de cuivre et (b) des couches diélectriques contenant surtout au moins une substance céramique sélectionnée parmi les substances représentées par les formules suivantes :

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba ; x et y sont dans le domaine polygonal délimité par 5 points A (x = 0,07, y = 0,15), B (x = 0,07, y = 0,07), C (x = 0,16, y = 0,07), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04 ;

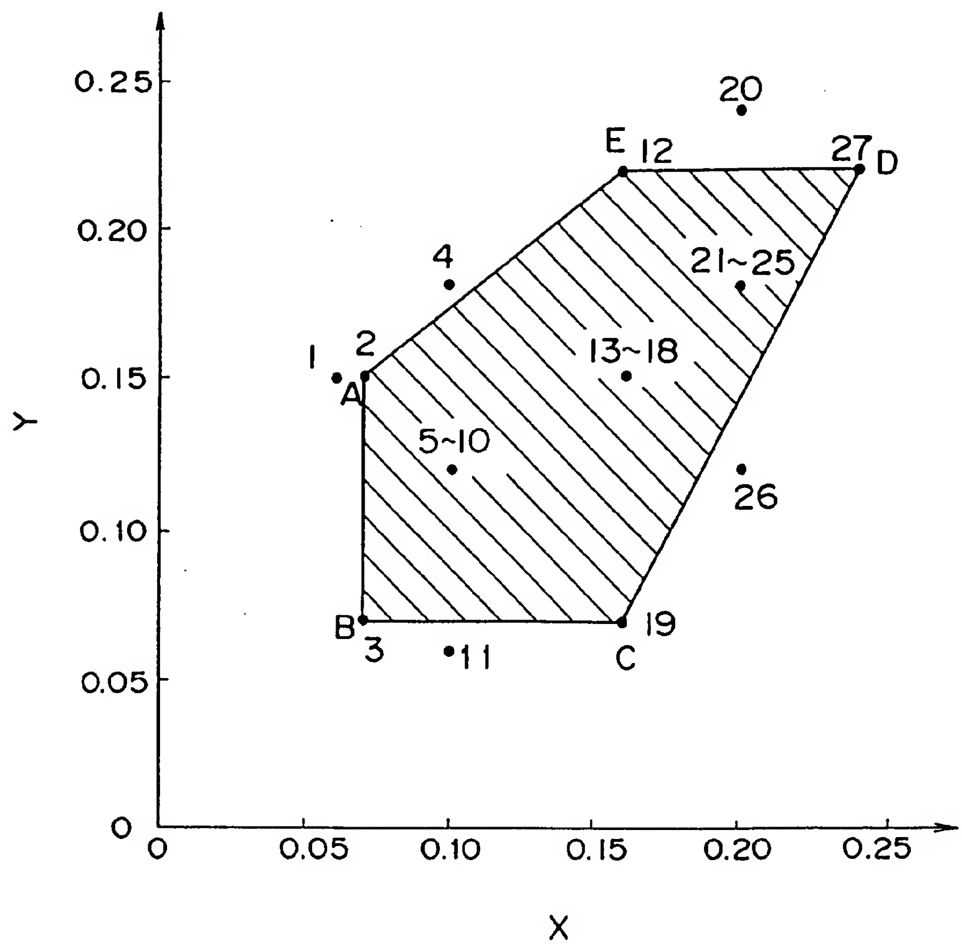
(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba ; x et y sont dans le domaine polygonal délimité par 5 points A (x = 0,07, y = 0,14), B (x = 0,07, y = 0,08), C (x = 0,18, y = 0.08), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04 ;

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

dans laquelle Me est au moins un élément choisi parmi Sr et Ba x et y sont dans le domaine polygonal délimite par 5 points A (x = 0,07, y = 0,16), B (x = 0,07, y = 0,09), C (x = 0,19, y = 0,09), D (x = 0,24, y = 0,22) et E (x = 0,16, y = 0,22) ; et 0 ≦ a ≦ 0,1, 0,02 ≦ b ≦ 1,0, 0,002 ≦ bz ≦ 0,04.

4. Condensateur en céramique à plusieurs couches selon la revendication 3, dans lequel au plus 85 % des atomes de Cu contenus dans les couches diélectriques sont remplacés par des atomes de Mn.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X
20
E
12
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D
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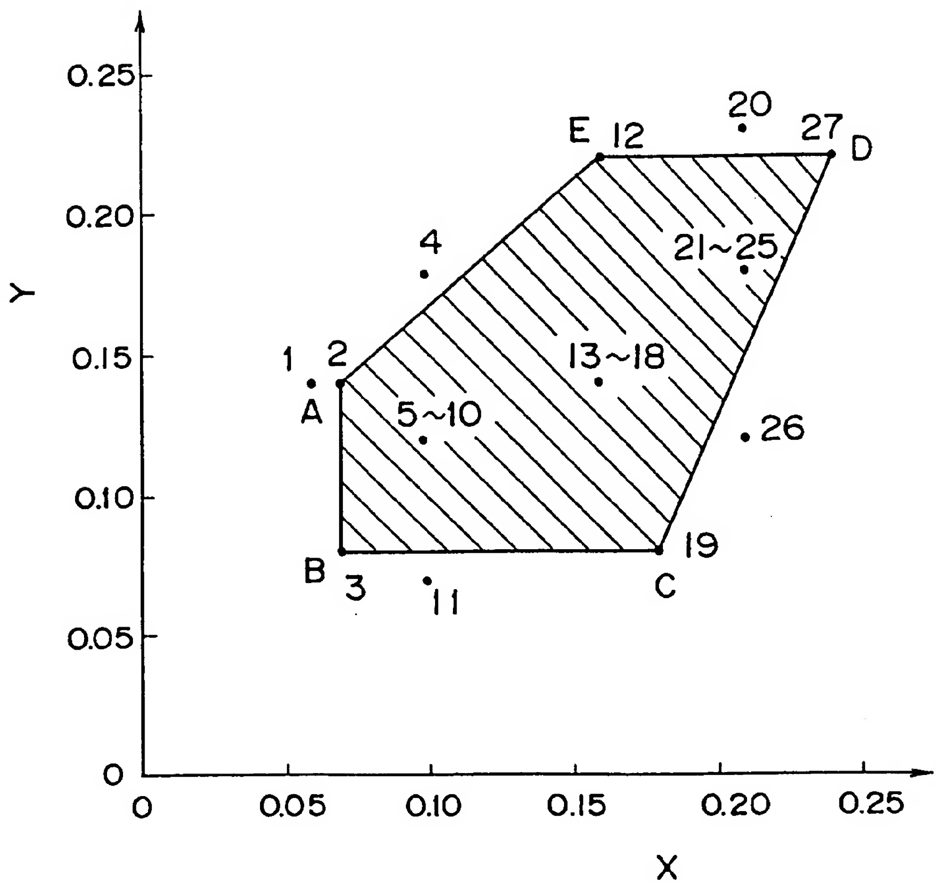
1
2
13~18
A
5~10
26
B
3
11
19
C

FIG.1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X
E
12
20
27
D
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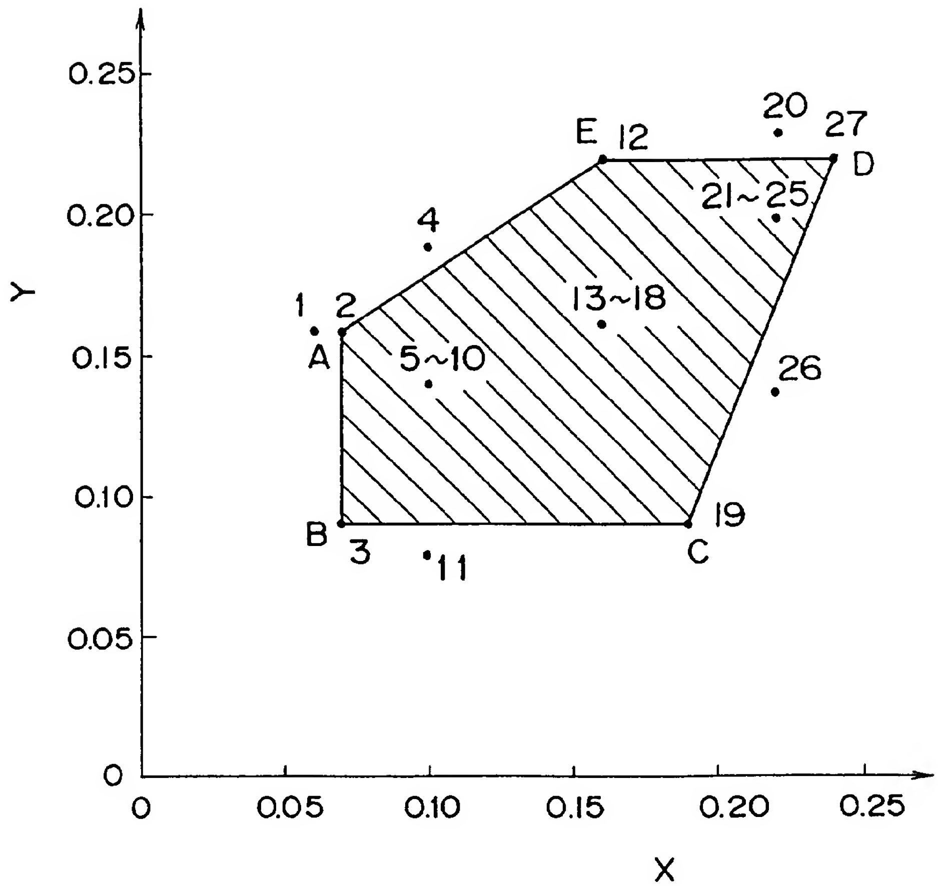
1
2
13~18
A
5~10
26
19
B
3
11
C

FIG. 2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0.20
0.25
E 12
20
27
D
21~25
4
1 2
A
13~18
5~10
26
B
3
11
C
19

FIG. 3

(Another Sheet)

(1) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bNb_{1-b})_z\}O_{3+a}$

(2) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bTa_{1-b})_z\}O_{3+a}$

(3) $Pb_{1-x+a}Me_x\{(Zn_{1/3}Nb_{2/3})_{1-y-z}Ti_y(Cu_bW_{1-b})_z\}O_{3+a}$

(1)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15}$
$\cdot((Cu_{1-c}Mn_c)_{1/3}Nb_{2/3})_{0.02}\}O_{3.02}$

(2)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15}$
$\cdot((Cu_{1-c}Mn_c)_{1/3}Ta_{2/3})_{0.02}\}O_{3.02}$

(3)' $Pb_{0.86}Sr_{0.16}\{(Zn_{1/3}Nb_{2/3})_{0.83}Ti_{0.15}$
$\cdot((Cu_{1-c}Mn_c)_{1/2}W_{1/2})_{0.02}\}O_{3.02}$